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# ESR STUDY OF THE DISTRIBUTION FUNCTION IN NEMATIC LIQUID CRYSTALS

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# ESR STUDY OF THE DISTRIBUTION FUNCTION IN NEMATIC LIQUID CRYSTALS

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ABSTRACT

Using vanadyl acetylacetonate as a paramagnetic probe, distribution function of nematic liquid crystals have been studied. It has been shown that position of spectral lines are not constant in supercooled nematic mesophase but they depend on the ordering of the liquid crystal and on the angle between the optic axis and the magnetic field direction. The influence of the magnetic field intensity on the ordering of the liquid crystal has been studied.

АННОТАЦИЯ

Используя ацетилацетонат ванадила в качестве парамагнитной пробы, нами была исследована функция распределения нематических жидких кристаллов. Показано, что в замороженной нематической мезофазе положение спектральных линий не постоянно, а зависит от упорядочения жидкого кристалла и от угла оптической оси с направлением магнитного поля. Изучено влияние магнитного поля на упорядочение жидкого кристалла.

KIVONAT

Vanadil acetilacetonát paramágneses próbát felhasználva vizsgáltuk nematikus folyadékkristályok eloszlási függvényét. Rámutattunk, hogy befagyasztott folyadékkristályos állapotban a spektrumvonalak helyzete nem állandó, hanem függ a folyadékkristály rendezettségétől és az optikai tengelynek a mágneses tér irányával bezárt szögétől. Mehatároztuk a mágneses térerő hatását a folyadékkristály rendezettségére.

## Introduction

It is possible to measure the ordering of nematic liquid crystals by ESR if paramagnetic test molecules are introduced into the liquid crystal. The best of these paramagnetic probes is vanadyl acetylacetonate. The degree of order can be measured by the change of its hyperfine constant as described in [1]. In this paper we report another way for determining the order parameter of liquid crystals by ESR. This method is based on the determination of the angular probability distribution function of the liquid crystal.

## The Distribution Function

If the distribution function is $F(\Theta)$, then $F(\Theta)d\Theta$ is the probability of finding a molecule with its long axis between $\Theta$ and $\Theta+d\Theta$ to the optic axis. As the simplest form of the distribution function we can take:

$$F(\Theta) = C \exp (a \sin^2\Theta) \qquad /1/$$

where

$$a = -q/kT$$

q is the activation energy.
The distribution function is connected with the anisotropic pseudo-potential U. The anisotropic pseudo-potential energy in a nematogen is defined as the average potential energy resulting from the interaction of one molecule with all the other molecules in the mesophase. This pseudo-potential can then be used to calculate any static property $\bar{\chi}$ of the liquid crystal, by taking the Boltzmann average:

$$\bar{\chi} = \frac{\int \chi(\omega) \exp(-U\beta) d\omega}{\int \exp(-U\beta) d\omega} \qquad /2/$$

where $\beta = 1/kT$

and $\omega$ is the solid angle describing the molecular orientation. Determination of the distribution function is therefore of central importance in understanding the properties of the nematic mesophase.

ESR Theory

In glassy state the ESR spectrum of vanidyl acetylacetonate /VACA/ is characteristic of a polycrystalline sample, i.e. the lines belonging to the parallel and perpendicular components of the hyperfine tensor show up separately. In supercooled nematic mesophase we also obtain the polycrystalline spectrum. Although the positions of the lines in the spectrum do not depend on the order of the liquid crystal, their intensities have a critical dependence on the angular probability distribution function.

Schwerdtfeger and Diehl [2] have shown that the intensities of the lines belonging to the parallel component of the hyperfine tensor can be used for the determination of the distribution function. The $M_I=^{7}/_{2}$ and $M_I=-^{7}/_{2}$ $A_{\parallel}$-lines are most distant from the intensive $A_{\perp}$-lines, so to eliminate the disturbing effect of these lines, we have to use the mentioned two $A_{\parallel}$-lines.

For the evaluation of the distribution function we need at least the two following spectra:

a/ when the magnetic field direction coincides with the optic axis of the liquid crystal;

b/ when the magnetic field direction is perpendicular to it.

Schwerdtfeger and Diehl [2] have used the following approximations in the solution of the problem:

1/ The intensity of the first low field $A_{\parallel}$-line is proportional to the distribution function;

2/ The polycrystalline spectrum of VACA contains singularities corresponding to absorption of microwave energy by molecules with their symmetry axis either parallel or perpendicular to the static magnetic field [4], and all the other molecules of the sample with different angles from 0 or $90^{\circ}$ make negligible contribution to these singularities;

3/ The transition probability does not depend on the angle of the V-O bond with the magnetic field direction.

Then the ratio of the amplitudes belonging to the orientations:

$$\frac{h_{\parallel 90^o}}{h_{\parallel 0^o}} = \frac{C \exp(a \sin^2 90)}{C \exp(a \sin^2 0)} = e^a \qquad /3/$$

i.e. we can obtain the $\underline{a}$ value characterizing the distribution function /1/.

James and Luckhurst gave a more detailed consideration of the problem. [3].

The orientation dependent resonant field $H_r(\Theta)$ for the transition

$$\left|\frac{1}{2}, M_I\right\rangle \leftrightarrow \left|-\frac{1}{2}, M_I\right\rangle \text{ is } [6, p.60]:$$

$$H_r(\Theta) = H_o - \frac{hKM_I}{g\beta} - \frac{h^2A_\perp^2}{4g^2\beta^2H_o}\left(\frac{A_\parallel^2+K^2}{K^2}\right)\left[I(I+1)-M_I^2\right] -$$

$$- \frac{h^2M_I^2}{2g^2\beta^2H_o}\left(\frac{A_\parallel^2-A_\perp^2}{K}\right)^2 \cdot \frac{g_\parallel^2 g_\perp^2}{g^4} \sin^2\Theta\cos^2\Theta \qquad /4/$$

where

$$g^2 = g_\parallel^2 \cos^2\Theta + g_\perp^2 \sin^2\Theta \qquad /5/$$

$$K^2g^2 = A_\parallel^2 g_\parallel^2 \cos^2\Theta + A_\perp^2 g_\perp^2 \sin^2\Theta \qquad /6/$$

$$H_o = \frac{h\nu}{g\beta} \qquad /7/$$

and $\Theta$ is the angle between the V-O bond and the magnetic field /Fig.1/.

The intensity of this transition at any value of the field H is:

$$h(\Theta,\varphi, H) = P(\Theta,\varphi) \cdot L(H, H_r, \sigma) \qquad /8/$$

where $L(H,H_r\sigma)$ is a line shape function with $\sigma$ peak-to-peak width of the line.

$P(\theta,\varphi)$ is the transition probability which, because of the anisotropic g-tensor, is also orientation dependent [5]:

$$P(\theta,\varphi) = \left(\frac{g_\perp}{g}\right)^2 \left\{ g_\parallel^2 + (g_\perp^2 - g_\parallel^2)\sin^2\theta\cos^2\varphi \right\} \qquad /9/$$

As the ESR spectrum of VACA in the supercooled liquid crystalline state is not a monocrystalline one, but there is a primary direction for the V-O bonds, the character of the spectrum is that between the monocrystalline and the glassy type ones. Thus

1/ The $A_\parallel$-lines show up separately from the $A_\perp$-lines;

2/ The intensity of the $A_\parallel$-lines depends on the angle between the magnetic field direction and the primary direction for the V-O bonds.

3/ The positions of the lines do not change.

Therefore the total intensity of the spectrum at the field H is obtained by integrating over all orientations of the probe and then summing over all values of the nuclear quantum number $M_I$, i.e.

$$h(H) = \sum_{M_I=-I}^{I} \int_0^{2\Pi} d\varphi \int_0^{\Pi} P(\theta,\varphi) \cdot L(H,H_r\sigma) \cdot F(\theta)\sin\theta d\theta \qquad /10/$$

As James and Luckhurst [3] have shown, this equation cannot be used in this form when the magnetic field direction and the primary direction of V-O bonds do not coincide. If these do coincide the distribution function /1/ has cylindrical symmetry about the magnetic field, otherwise the probability is a function of both $\theta$ and $\varphi$ /Fig.1/.

The probability of finding a molecule with its V-O bond at an angle between $\alpha$ and $\alpha+d\alpha$ to the optic axis is $F(\alpha)d\alpha$. As it can be seen from Fig.1

$$\cos\alpha = \cos\theta\cos\gamma + \sin\theta\sin\gamma\sin\varphi \qquad /11/$$

where $\gamma$ is the angle between the optic axis and the magnetic field direction /the angle of rotation/.

The final result for the intensity of the spectrum at any angle of rotation and any field H is:

$$h(H)=\sum_{M_I=-I}^{I}\int_{o}^{2\Pi}d\varphi\int_{o}^{\Pi}P(\theta,\varphi)\ .\ L(H,H_r\sigma).$$

$$.\ F\left[\arccos\left(\cos\theta\cos\gamma+\sin\theta\sin\gamma\sin\varphi\right)\right]\sin\theta d\theta \qquad /12/$$

It follows that if Schwerdtfeger and Diehl's analysis is correct, the ratio of the $F(\gamma)$ probability distribution /where $F(\gamma) = C\exp(a\sin^2\gamma)$ / to the spectral intensity should be independent of the angle $\gamma$. As James and Luckhurst [3] have shown, this situation is not realized so they determined the dependence of $F(\gamma)/h_{\parallel}$ on the angle of rotation and have shown the method of determination of the distribution function. As to the form of the distribution function they assumed

$$F(\alpha) = C\exp(a\sin^2\theta + b\sin^4\theta) \qquad /13/$$

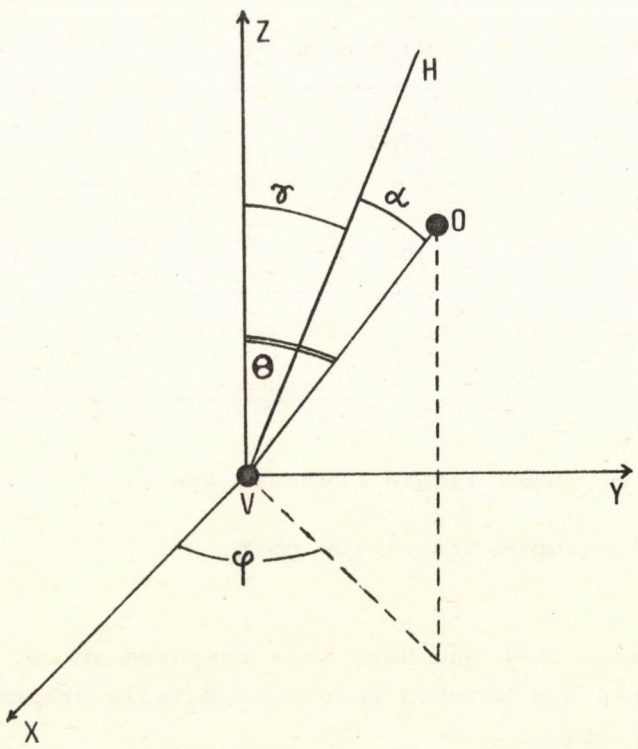



Fig.1. The orientation of the V-O bond in a laboratory axis system

Experimental

We have been studying ESR spectra of VACA dissolved in the following liquid crystals:

EMAB /p-ethyl-p'-methoxy-azoxybenzene/

Merck-4

Merck-5

MBBA /p-methoxybensilidene-p'-buthylaniline/.

Table 1.

| Liquid crystal | $T_c^{**}$ °C pure liquid crystal | $T_c$ °C liquid crystal + $10^{-3}$ M VACA |
|---|---|---|
| EMAB | 71.5 | 69.0 |
| MBBA | 47.0 | 44.0 |
| Merck-4* | 76.0 | 74.0 |
| Merck-5* | 76.0 | 74.0 |

*For the composition of these liquid crystals see [1].

**$T_c$ is the nematic-isotropic transition point.

Liquid crystals EMAB and MBBA were prepared in our institute, liquid crystals Merck-4 and Merck-5 were commercially prepared and obtained from the Merck Organisation.

The mole fraction of VACA was always less than $10^{-3}$, and the samples were degassed several times before being sealed off under vacuum.

The ESR spectra were performed at 9.2. KMHz and 100 KHz field modulation. Field position were measured to an accuracy of $\pm$ 0.1 G with a proton magnetometer.

The theoretical heights of the spectral lines were calculated on an ICT-1905 computer using the Simpson approximate formula of integration.

## Results and Discussion

Since James and Luckhurst's values of the components of hyperfine and g-tensors were very much different from the values determined by us, the intensities of $A_{\parallel}$-lines were calculated as a function of the angle of rotation and the form of $F(\gamma)/_{h_{\parallel}} = f(\gamma)$ function was determined using Eq./12/. The line shape function $L(H,H_r\sigma)$ was taken to be gaussian. The linewidth and the measured A - and g-values were varied until the best agreement between lineshapes of the theoretical experimental spectra was obtained. As a result of this the peak-to-peak linewidth was taken to be $\sigma$ = 14 gauss and the following A - and g-values were obtained:

Table 2.

| | |
|---|---|
| $g_{\perp}$ = 1.981 | $A_{\perp}$ = 190.0 MHz |
| $g_{\parallel}$ = 1.945 | $A_{\parallel}$ = 506.8 MHz |

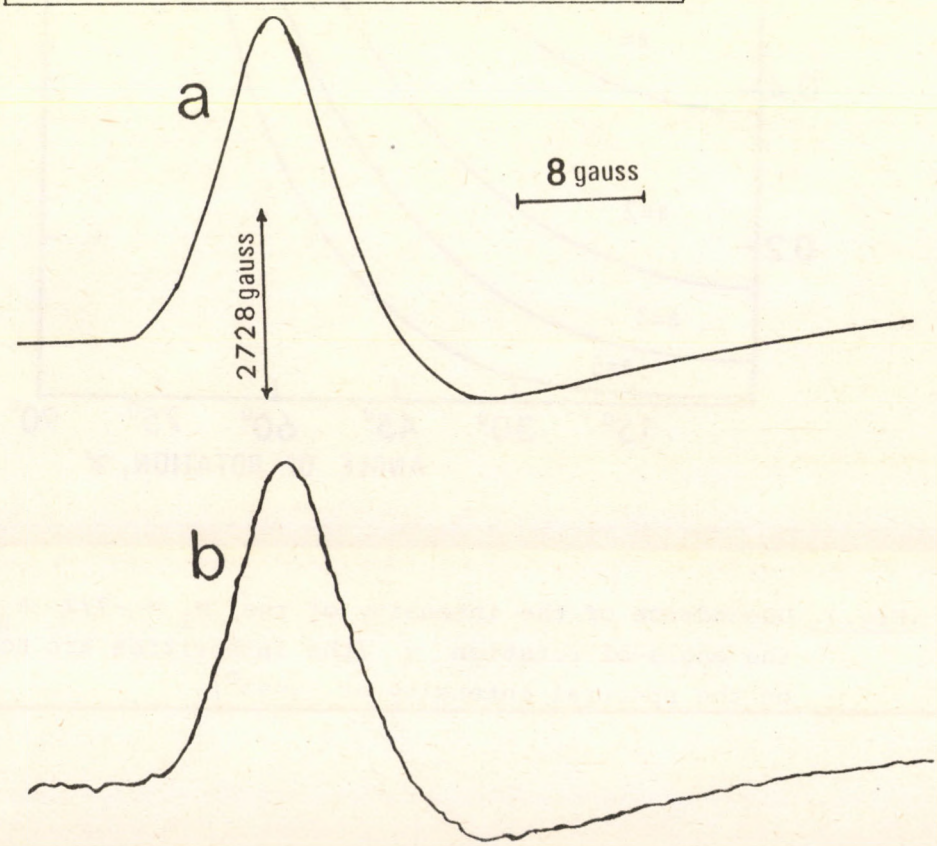



Fig.2. Theoretical /a/ and experimental /b/ shapes of the first low field $A_{\parallel}$-line at $\gamma=90^{o}$ /the value of parameter in Eq. /1/ equals 3/

The calculation shows that only the $M_I = 7/2$ and $M_I = -7/2$ $A_{||}$-lines can be used for the determination of the distribution function. The other $A_{||}$-lines are overlapped by much more intensive $A_{\perp}$-lines, so a simple intensity dependence cannot be obtained for them and the intensities of the A -lines are described by another distribution function:

$$\int_0^{2\Pi} F\left[\arccos\left(\sin\gamma\sin\varphi\right)\right] d\varphi \qquad /14/$$

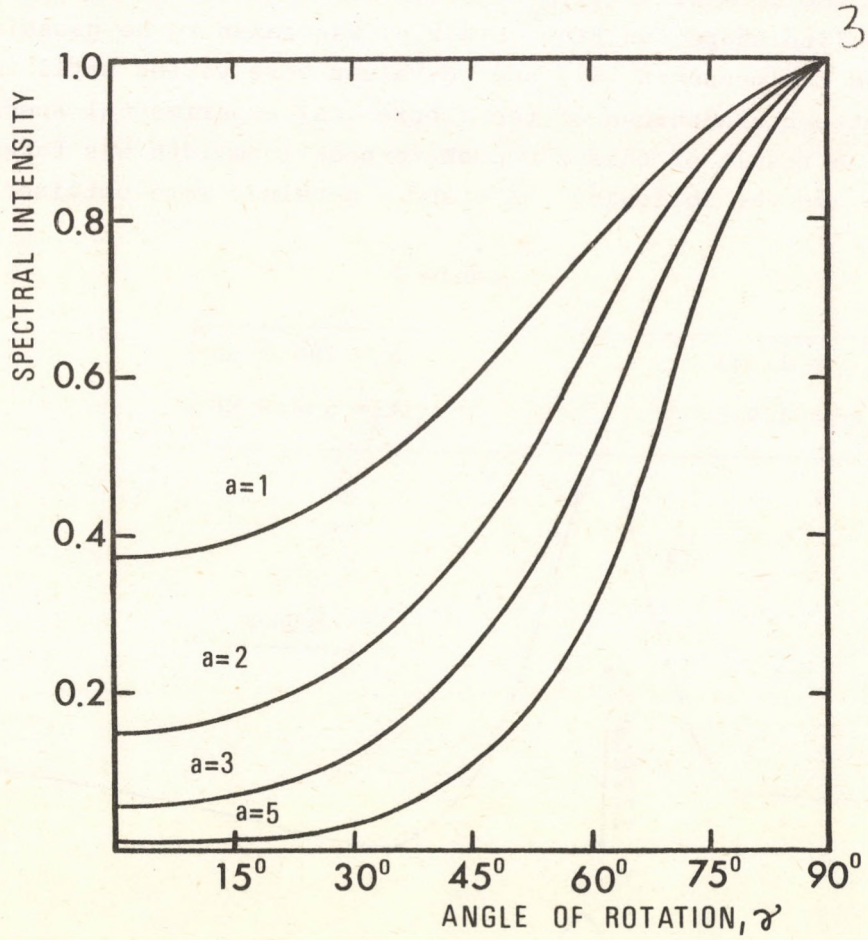
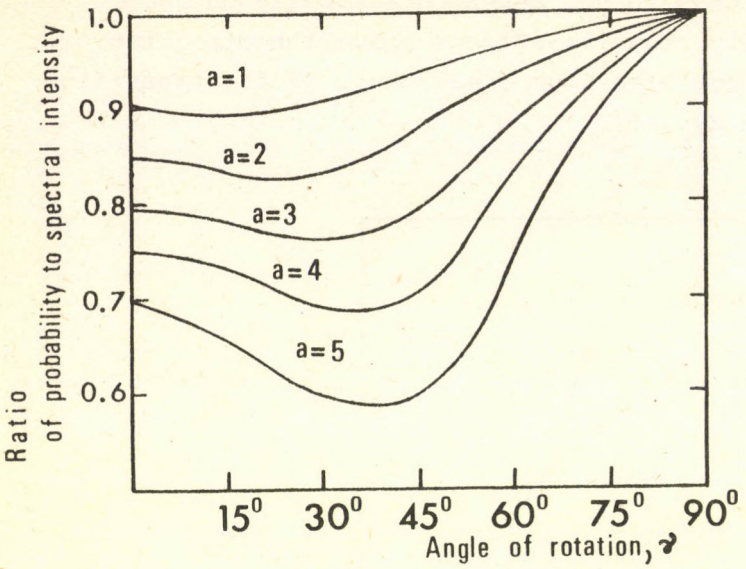
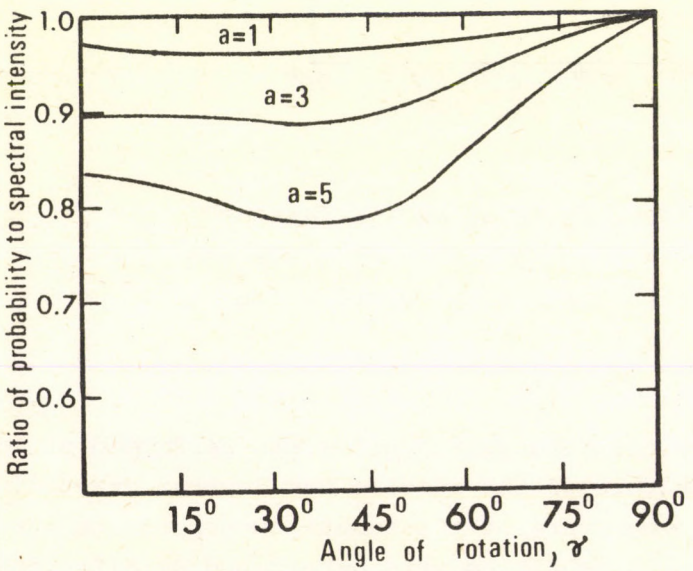



Fig.3. Dependence of the intensity of the $M_I = -7/2$ $A_{||}$-line on the angle of rotation $\gamma$ /the intensities are normalized on the spectral intensity at $\gamma=90^{\circ}$/




4a.




4b.

Fig.4. Dependence of $F(\gamma)/h_{\parallel}$ on the angle of rotation $\gamma$ for $M_I=-7/2$ $A_{\parallel}$-line in the case of $\sigma$ = 14 gauss peak-to-peak linewidth /a/ and of $\sigma$ = 7 gauss linewidth /b/

The obtained results are very close to those determined by James and Luckhurst, although the magnetic parameters differ strongly from theirs. However, the following should be noted:

1/ The dependence of $F(\gamma)/h_{\parallel}$ function on the angle of rotation decreases gradually with the decrease of the linewidth /Fig.4/ and at $\sigma$ = 0.2 G width practically no dependence can be obtained / theoretically this can be realized at an infinitesimal linewidth/. One can see that all of Schwerdtfeger and Diehl's assumptions are identical to the following: the distribution function is proportional to the first low field $A_{\parallel}$-line intensity in the case of the infinitesimal linewidth.

2/ The peak position of the spectral lines is not constant but depends on the angle of rotation and the parameter of the distribution function /1/ /Fig.5/. The change of the peak position at a = 5 for the $M_I=-7/2$ $A_{\parallel}$-line can reach already about 3 gauss. Since liquid crystals are often used as solvents for anisotropy determination in magnetic resonance experiments, the accuracy of measured A-values for different radicals is lower than was assumed.

3/ The spectral intensities do not depend practically on the transition probability. That is evident since the direction dependent terms can reach maximum 4 per cent. of the transition probability value in Eq. /9/.

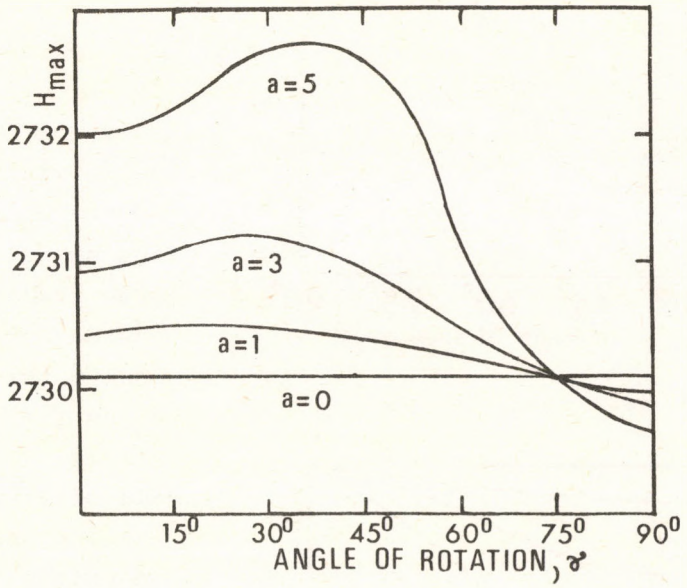



Fig.5. Dependence of the position of the peak of the $M_I$=-7/2 $A_\parallel$-line on the angle of rotation at different values of parameter a in Eq. /1/

The determination of the distribution function was performed at low temperature /∿-160°C/. The temperature of the samples was lowered gradually in the magnetic field from the temperature of the nematic mesophase to that of the experiment and the spectral intensities were determined at different values of the angle of rotation. It is clear that using this method the highest degree of order can be measured. Our experiments show that the rate of the temperature decrease has a strong influence on the measured order parameter. If the cooling is very rapid, the liquid crystal freezes before being able to reach its maximum ordering. If the cooling is too slow, the anisotropy decreases again, this time at a rate of about 1°C per minute the liquid crystal changes to a disordered polycrystal, thereby indicating that the spectral intensities do not depend on the angle of rotation. The optimum rate of cooling at which the liquid crystal reaches its maximum ordering and does not crystallize, was found to be 4-5°C per minute. James and Luckhurst [3] investigated a liquid crystalline mixture at a low temperature.

They found a quartic term in the distribution function /13/, the cause of which they put down either to the low temperature or to the mixing liquid crystals. In our opinion the appearance of the quartic term is the consequence of mixing liquid crystals of different structure, since in unicomponent liquid crystals we studied no quartic term was found and the distribution function /1/ in all cases described correctly the spectral intensity changes.

The order parameter values from the distribution function can be obtained by the formula

$$O_{zz} = \frac{\int_0^{\Pi} \frac{3\cos^2\alpha - 1}{2} F(\alpha) \sin\alpha d\alpha}{\int_0^{\Pi} F(\alpha)\sin\alpha d\alpha} \qquad /15/$$

The determination of order parameter values was performed at different magnetic field intensities /Fig.6/. It can be seen that liquid crystals EMAB, Merkc-4 and Merck-5 reach their maximum alignment at about 4 kG, but for the maximum ordering of MBBA a field intensity of about 5.5 kG is necessary.

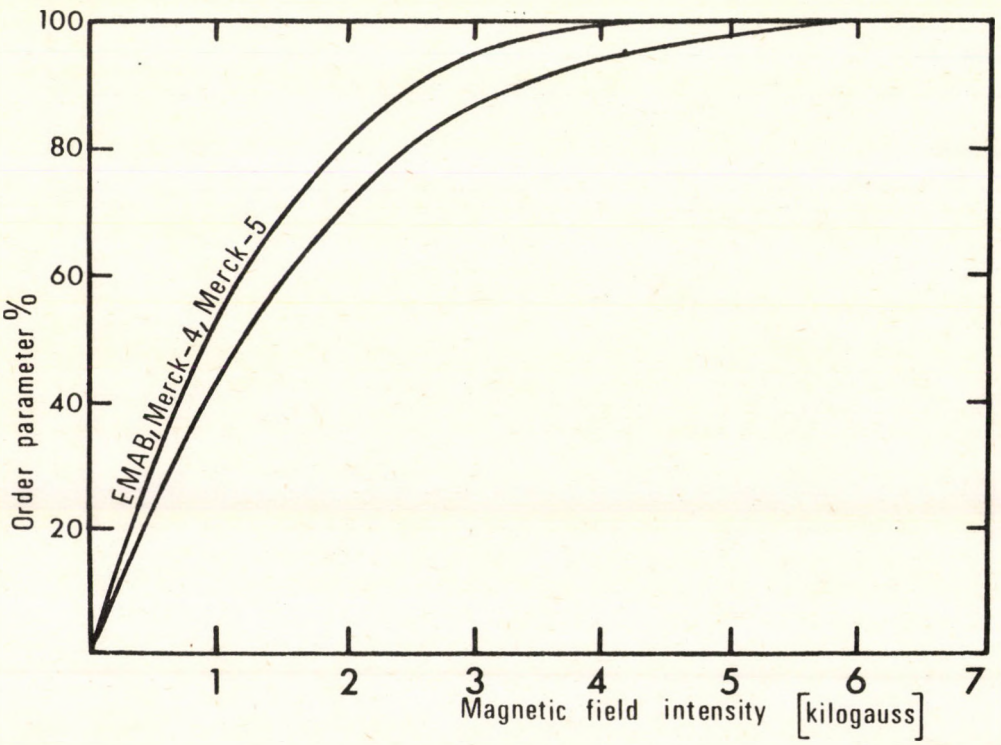



Fig.6

Liquid crystal p-azoxyanisole reaches its maximum alignment in a magnetic field of $\sim$2 kG [7]. We assume that the higher intensity of the magnetic field in our case is the consequence of high viscosities of these liquis crystals.

The order parameter values obtained from the determination of the distribution function /at about 3300 G/are compared with those evaluated from the distance of $M_I$=-3/2 and $M_I$=-1/2 lines in the nematic mesophase [1]. The results shown by Table 3 are in satisfactory agreement. The order parameter values determined from the distribution function are in all cases lower /due to the slight deformation of $M_I$=-3/2 and $M_I$=-1/2 lines/. A significant difference for MBBA can be seen, probably because of its very high viscosity.

Table 3.

| Liquid crystal | $O_{zz}$ from [1] | $O_{zz}$ from the distribution function |
|---|---|---|
| EMAB | - 0.385 | - 0.365 |
| MBBA | - 0.400 | - 0.331 |
| Merck-4 | - 0.410 | - 0.380 |
| Merck-5 | - 0.415 | - 0.387 |

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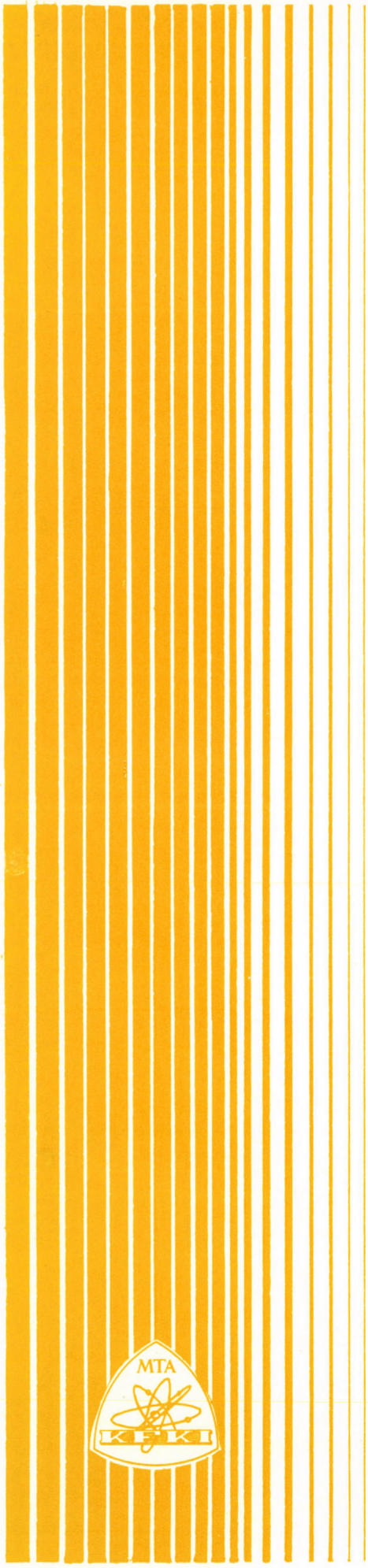


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